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Alkali Leaching of Antimony Sulphide and Electrolytic Recovery of Antimony from the Resulting Leach Solution

Vincent J. Andrews

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AND
ELECTROLYTIC RECOVERY OF ANTIMONY
FROM THE
RESULTING LEACH SOLUTION

by
Vincent J. Andrews

A Thesis
Submitted to the Department of Metallurgy
in Partial Fulfillment of
the Requirements for the Degree of
Bachelor of Science in Metallurgical Engineering

Montana School of Mines
Butte, Montana
May 7, 1938
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INTRODUCTION

Stibnite (Sb₂S₃), antimony sulphide or glance, is the chief mineral from which antimony is extracted. Up to the present time dry methods have been generally adopted for the extraction of antimony from Stibnite. The wet and electrolytic methods have received much attention in Europe and America, but have yet found no practical applications.

There have been several proposals for the extraction of antimony from its ores electrolytically. Borches¹) proposed a method using a sodium sulphide solution as the solvent for Stibnite to form a solution of sulphantimonite and sulphantimonate and electrolyzing the solution by the use of insoluble anodes.

Koepp² leached the Stibnite with a solution of ferric chloride according to the equation:

\[ 6 \text{FeCl}_3 + \text{Sb}_2\text{S}_3 = 6\text{FeCl}_2 + 2 \text{SbCl}_3 + 3\text{S} \]

and electrolyzed the solution at 50°C, using lead electrodes.

Siemens and Halske³ extracted antimony from Stibnite with alkali sulphides, hydrosulphides, or polysulphides. The Stibnite was brought into solution in the form of a double salt that is with NaHS

\[ 3 \text{Sb}_2\text{S}_3 + 6 \text{NaHS} = 6 \text{NaSbS}_2 + 3 \text{H}_2\text{S} \]

¹. Electro-Metallurgie p. 148 Braunschweig 1891
². Handbook of Metallurgy Vol. 2 by Schnabel
³. German Patent, No. 67, 973 June 29, 1892
The liquor was then electrolyzed in diaphragm chambers with carbon or platinum anodes and copper or antimony cathodes. Siemens also used alkaline earth sulphides as the solvent. No practical applications appear to have been made of these processes.

D. J. Demorest\(^1\) made some experiments on a small scale at Ohio State University using an 8\% sodium hydroxide solution as the electrolyte. The antimony was deposited on 12 x 12 inch cathodes suspended in a tank 60 x 18 x 18 inches using a current density of 7 amperes per square foot at 2.7 volts.

The drawbacks to the process were the comparatively low solubility of antimony in the electrolyte and the accumulation of the sulphur in the solution which decreased the solvent power of the solution and destroyed the iron anodes.

As a result of these experiments a plant was built on a large scale capable of treating 600 pounds of antimony per day at a current efficiency of 76\%. The electrolyte was regenerated or renewed when the anodes were attacked. No great commercial success appears to have favored the enterprise.

\[\text{1. Journal of American Institute of Metal, Vol. XI, No.1}\]
The electrolytic method of extracting antimony is chiefly desired for treating low grade antimony ores and residues where other methods cannot be used economically.

It is the purpose of this investigation to obtain some insight into optimum conditions for leaching Stibnite with sodium hydroxide solution and also to study the factors affecting the electrolysis of the resulting solution.
EXPERIMENTAL

To study the effects of concentration of solution, time of leaching, temperature of leaching, amount of solute, and the roasting of Stibnite before leaching on the extraction of antimony from Stibnite by leaching, the following experiments were performed. The Stibnite used in the experiments was purchased from the Merk Chemical Company and contained a small amount of arsenic. The leaching solution was made by dissolving the required amount of stick sodium hydroxide in the required amount of distill water.

The Effect of Concentration

The leaching experiments were carried out in 400 & C beakers. A four gram sample of stibnite was weighed out and placed in the beaker with 250 & C of sodium hydroxide solution. The concentration of sodium hydroxide solution used consisted of 15, 30, 60, and 120 grams per 1,000 c c of water. The contents of the beaker were stirred frequently with a stirring rod. The temperature was kept constant. At the end of a half-hour, the mixture was immediately filtered through a laboratory vacuum filter and 2-25 c c portions of the filtrate were pipetted and analyzed for antimony,
Using Low's\textsuperscript{1} permanganate method. Knowing the original volume of the solute and amount of stibnite used, the percentage extraction is easily calculated.

The reaction which takes place during the solution of stibnite in sodium hydroxide is:

\[
\text{Sb}_2\text{S}_3 + 2\text{NaOH} \rightarrow \text{NaSbS}_2 + \text{NaSbO}_3 + \text{H}_2\text{O}
\]

according to D. J. Demorest\textsuperscript{1} and others.

The results obtained are shown tabulated in table 1, and graphically represented in figures 1, 2, & 3. All determinations were done in duplicate and the average of the results taken.

Table 1.—The Effect of Concentration on Extraction

<table>
<thead>
<tr>
<th>Concentration of NaOH in grams per liter</th>
<th>Extraction Leaching Time</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(\frac{1}{2}) hour</td>
</tr>
<tr>
<td>15</td>
<td>23%</td>
</tr>
<tr>
<td>30</td>
<td>30%</td>
</tr>
<tr>
<td>60</td>
<td>70%</td>
</tr>
<tr>
<td>120</td>
<td>71%</td>
</tr>
</tbody>
</table>

1. Technical Methods of Ore Analysis by Low
**Fig. I - Effect of Concentration on Extraction**

Time of leaching $\frac{1}{2}$ hour,
Temperature $20^\circ$ C.
Quantity of stibnite used 4 grams
Quantity of solution 250 C C
Variable concentration
Fig. II - Effect of Concentration on Extraction

Time of leaching 1 hour
Temperature 20° C.
Quantity of stibnite used 4 grams
Quantity of solution 250 C C
Variable concentration
Concentration - grams Na OH/liter

Fig. III - Effect of Concentration on Extraction

Time of leaching 2 hours
Temperature 20°C
Quantity of Stibnite used 4 grams
Quantity of solution 250 CC
Variable concentration
From the plotted results, it is readily seen that the maximum extraction is obtained with a concentration of 60 grams per liter. Using higher concentrations than 60 grams has no effect on extraction and weaker concentrations lower the extraction.

Therefore the effect of time on extraction was determined for these solutions.

**Effect of Leaching Time**

In determining the effect of time on extraction similar procedure was followed as in the preceding determinations. In this case, however, time was the variable. The concentration and temperature were kept constant for each set of determinations.

Results are given in table II and illustrated graphically in figures 3 and 4.

**Table II.**--The Effect of Time on Extraction.

<table>
<thead>
<tr>
<th>Concentration of solvent 60 and 120 grm/liter</th>
<th>Temperature 20°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quantity Stibnite used 4 grams</td>
<td></td>
</tr>
<tr>
<td>Quantity of solution 250 c c</td>
<td></td>
</tr>
<tr>
<td>Variable time</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Time in Minutes</th>
<th>Con. of leaching solution 60 gms/liter</th>
<th>120 gms/liter</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>37%</td>
<td>79%</td>
</tr>
<tr>
<td>30</td>
<td>70%</td>
<td>71%</td>
</tr>
<tr>
<td>60</td>
<td>72%</td>
<td>71%</td>
</tr>
<tr>
<td>120</td>
<td>72%</td>
<td>85%</td>
</tr>
</tbody>
</table>
Fig. IV - Effect of Time on Extraction

Concentration of solvent -- 60 grams/liter
Temperature -- 20°C.
Quantity of Stibnite used 4 grams
Quantity of solution 250 cc
Variable time
Fig. V - Effect of Time on Extraction

Concentration of solvent -- 120 grams / liter
Temperature -- 20° C.
Quantity of Stibnite used 4 grams
Quantity of solution 250 c c
Variable time
It is apparent from the curves and table that time has no marked effect on the extraction.

The Effect of Temperature

The procedure in obtaining these results was again similar to the previous determinations. The leaching at 0°C was done by immersing the beaker containing the sodium hydroxide solution in a freezing mixture of snow and salt until the solution became the same temperature as the bath when the Stibnite was introduced. The 10°C leach was done in a similar manner except instead of using snow and salt, tap water was used whose temperature was 10°C. The 40°C leach was accomplished in a Freas water thermostat. The leach at 96°C was performed by heating the leach solution to boiling on a hot plate. The solution was kept covered with a watch glass to prevent excessive evaporation. When the solution boiled, the Stibnite was introduced cautiously and allowed to boil several minutes. It was then immediately filtered and same procedure followed as in the previous experiments.

The results obtained are shown in table 3, and represented graphically in figure 6.
Temperature in Degrees Centigrade

Fig. VI - Effect of Temperature on Extraction

Concentration of solvent--60 grams / liter
Time of leaching $\frac{1}{2}$ hour
Quantity of Stibnite used 4 grams
Quantity of solution 250 c c
Variable temperature
Table IV.--The Effect of the Amount of Stibnite Placed in Solvent.

Concentration of solvent 60 grams / liter
Time of leaching 1 hour
Temperature 20° C.
Quantity of solution 250 c c
Variable amount of Stibnite used

<table>
<thead>
<tr>
<th>Amount of Stibnite used</th>
<th>Percentage Extracted</th>
<th>Grams of Sb per Liter of Solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>75%</td>
<td>2.10</td>
</tr>
<tr>
<td>2</td>
<td>73%</td>
<td>4.10</td>
</tr>
<tr>
<td>3</td>
<td>70%</td>
<td>5.95</td>
</tr>
<tr>
<td>4</td>
<td>71%</td>
<td>8.35</td>
</tr>
<tr>
<td>8</td>
<td>37%</td>
<td>8.60</td>
</tr>
</tbody>
</table>

From the results obtained it is apparent that the more Stibnite there is introduced into the solution the greater is the amount that goes into the solution up to a certain point. This is the principle of the law of mass action which holds until the solution becomes saturated with antimony. In this case the solution is saturated with antimony when it contains 8.6 grams per liter.

It is apparent that the high extractions obtained in the preceding determinations are misleading since small amounts of Stibnite were used. It should be noted that the amount of antimony that NaOH will hold in solution is limited and very small.
Table III.--The Effect of Temperature on Extraction.

Concentration of Solvent 60 grams / liter
Time of leaching ½ hour
Quantity of Stibnite used 4 grams
Quantity of solution 250 c c
Variable Temperature

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Per Cent of Extraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Degrees Centigrade</td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>20%</td>
</tr>
<tr>
<td>10</td>
<td>25%</td>
</tr>
<tr>
<td>20</td>
<td>74%</td>
</tr>
<tr>
<td>40</td>
<td>74%</td>
</tr>
<tr>
<td>97</td>
<td>89%</td>
</tr>
</tbody>
</table>

The examination of the table and curves reveal that temperatures above 20° C. have no marked effect on the extraction.

Effect of the Amount of Stibnite Used

Similar procedure was carried as in the preceding experiments. All factors were kept constant except the amount of Stibnite introduced into the solution. The amount of Stibnite used per 250 c c of solvent was 1, 2, 3, 4, and 8 grams.

The results obtained are shown in table 4 and figure 7.
Fig. VII - Effect of Amount of Stibnite on Extraction

Amount of Stibnite in Grams

Concentration of solvent -- 60 grams / liter
Time of leaching 1 hour
Temperature -- 20°C
Quantity of solution 250 c.c.
Variable quantity of Stibnite used
Amount of Stibnite in Grams

Fig. VIII - Amount of antimony grams / liter

Concentration of solvent--60 grams / liter
Time of leaching 1 hour
Temperature--20°C.
Quantity of solution 250 c c
Variable quantity of Stibnite used
Effect of Roasting

The roasting of the Stibnite was done in small roasting dishes in a gas muffle furnace. Ten grams of Stibnite were weighed out, placed in each of four small roasting dishes and roasted in the furnace with continuous rabblling and a plentiful supply of air. The temperatures of roasting were 340° C. and 400° C. A small dish of the roasted Stibnite was taken from the furnace at fifteen minute intervals.

Table V.--The Effect of Roasting on Extraction

<table>
<thead>
<tr>
<th>Concentration of Solvent 60 grams</th>
<th>Time of leaching ½ hour</th>
<th>Temperature 20° C.</th>
<th>Quality of Roasted Ore 4 grams</th>
<th>Quality of Solvent 250 c c</th>
</tr>
</thead>
<tbody>
<tr>
<td>Time of Roasting Antimony in grams / liter</td>
<td>Temperature of Roasting 250</td>
<td>400</td>
<td></td>
<td></td>
</tr>
<tr>
<td>in Minutes</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>.2</td>
<td>.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>.4</td>
<td>.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>45</td>
<td>.4</td>
<td>.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>60</td>
<td>.7</td>
<td>.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pure Sb₂O₃</td>
<td>.7</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

In order to determine the effect of roasting on extraction, the roasted sulphide was leached with NaOH.
The leaching was done as in preceding determination. The results obtained are shown in table 5.

From table 5, it is readily seen that the roasting of the ore does not aid in increasing the amount of antimony in solution.

**Electrolysis**

A few electrolyzing experiments were carried out to determine the effect of current density on character of deposit and current efficiency. For this purpose a solution obtained from leaching Stibnite with 60 grams of NaOH / liter was used. It contained 8.6 grams of Sb / liter. The electrolyzing was done in a 250 cc beaker using lead anode and cathode at an E. M. F. of 2.75 volts and various current densities.

The results obtained are given in table 6.

**Table VI. -- The Effect of Current Density on Nature of Deposit and Current Efficiency.**

<table>
<thead>
<tr>
<th>C. D. in Amps / Sq. Ft.</th>
<th>Current Efficiency</th>
<th>Nature of Deposit</th>
</tr>
</thead>
<tbody>
<tr>
<td>9</td>
<td>77%</td>
<td>black not</td>
</tr>
<tr>
<td>16</td>
<td>84%</td>
<td>very</td>
</tr>
<tr>
<td>22</td>
<td>79%</td>
<td>very</td>
</tr>
<tr>
<td>28</td>
<td>58%</td>
<td>coherent</td>
</tr>
<tr>
<td>33</td>
<td>79%</td>
<td>coherent</td>
</tr>
</tbody>
</table>
From table VI the current efficiency does not show any relationship to the current density. This is probably due to the fact that the incoherent deposit of antimony fell off from the cathodes during electrolysis giving the erratic results for current efficiency.

The Electrolyte did not seem to affect the lead electrodes. The surface of the anode became coated with PbO₂ apparently which protects the lead from attack of the electrolyte.
SUMMARY

1. Antimony sulphide is leached with sodium hydroxide using various solvent concentrations, leaching time, and temperature. The maximum solubility of antimony in sodium hydroxide is 8.60 grams of antimony per liter of 6% NaOH solution at room temperature.

2. Temperature changes above room temperature do not appreciably affect the solubility.

3. Time of leaching has no affect on the extraction.

4. Roasting of the Stibnite previous to the leaching decreases the extraction and the amount of antimony in solution.

5. The antimony from the leach solution can be precipitated with an electric current using lead electrodes at a current efficiency of approximately 75%.
ACKNOWLEDGEMENTS

I wish to acknowledge my indebtedness to Dr. Curtis L. Wilson, Professor of Metallurgy, Montana School of Mines, and to Dr. Ettore A. Peretti, Instructor of Metallurgy, Montana School of Mines, for their advice and helpful suggestions during the progress of my research; also to Prof. L. J. Hartzell, Professor of Chemistry, Montana School of Mines, for his assistances and advise in the analytic work.